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(54) Title of the Invention

Resin composition and multilayered structure using
the same

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Specification

1. Title of the Invention

Resin composition and multilayered structure using the same

2. Scope of the Claims

(1) A resin composition comprising from 94 to 30 parts by weight of a saponified product(A) of an ethylene-vinyl acetate copolymer having an ethylene content of from 20 to 45 mol%, and a degree of saponification of the vinyl acetate component of 96 mol% or more, and from 6 to 70 parts by weight of a saponified product(B) of an ethylene-vinyl acetate copolymer having an ethylene content of from 24 to 49 mol%, and a degree of saponification of the vinyl acetate component of less than 96 mol%, and satisfying the following formulas (I) to (III):

Ethylene content of (B) - Ethylene content of (A) \geq 4 mol% ... (I)

Degree of saponification of (A) - Degree of saponification of (B) \geq 3 mol% ... (II)

$1.5 + \{50 - \text{Ethylene content of (B)}\} \times 0.06 \geq |\text{SP(A)} - \text{SP(B)}|$
 $\geq \{\text{Ethylene content of (B)} - 38\} \times 0.04 + 0.1$... (III)

provided that

SP(A)... Solubility parameter of A (according to Small's equation)

SP(B)... Solubility parameter of B (according to Small's equation)

(2) The resin composition according to claim 1, which satisfies the following formulas (I') and (III'):

$25 \text{ mol\%} \geq \text{Ethylene content of (B)} - \text{Ethylene content of (A)} \geq 4 \text{ mol\%} \dots (\text{I}')$

$20 \text{ mol\%} \geq \text{Degree of saponification of (A)} - \text{Degree of saponification of (B)} \geq 3 \text{ mol\%} \dots (\text{II}')$, and

$1 + \{50 - \text{Ethylene content of B}\} \times 0.06 \geq |\text{SP(A)} - \text{SP(B)}| \geq \{\text{Ethylene content of (B)} - 38\} \times 0.01 + 0.2 \dots (\text{III})'$

(3) A multilayered structure having a thermoplastic resin layer on at least one surface of a layer of a resin composition comprising from 94 to 30 parts by weight of a saponified product(A) of an ethylene-vinyl acetate copolymer having an ethylene content of from 20 to 45 mol%, and a degree of saponification of the vinyl acetate component of 96 mol% or more, and from 6 to 70 parts by weight of a saponified product(B) of an ethylene-vinyl acetate copolymer having an ethylene content of from 24 to 49 mol%, and a degree of saponification of the vinyl acetate component of less than 96 mol%, and satisfying the following formulas (I) to (III):

$\text{Ethylene content of (B)} - \text{Ethylene content of (A)} \geq 4 \text{ mol\%} \dots (\text{I})$

$\text{Degree of saponification of (A)} - \text{Degree of saponification of (B)} \geq 3 \text{ mol\%} \dots (\text{II})$

$1.5 + \{50 - \text{Ethylene content of (B)}\} \times 0.06 \geq |\text{SP(A)} - \text{SP(B)}| \geq \{\text{Ethylene content of (B)} - 38\} \times 0.04 + 0.1 \dots (\text{III})$

(4) The multilayered structure according to claim 3, which satisfies the following formulas (I') and (III'):
 $25 \text{ mol\%} \geq \text{Ethylene content of (B)} - \text{Ethylene content of (A)} \geq 4 \text{ mol\%} \dots (\text{I}')$

$20 \text{ mol\%} \geq \text{Ethylene content of (A)} - \text{Ethylene content of (B)} \geq 3 \text{ mol\%} \dots (\text{II}')$, and

$1 + \{50 - \text{Ethylene content of B}\} 0.06 \geq |\text{SP(A)} - \text{SP(B)}| \geq \{ \text{Ethylene content of (B)} - 38 \} \times 0.01 + 0.2 \dots (\text{III}')$

(5) The multilayered structure according to claim 3, wherein the thermoplastic resin is selected from polypropylene resins, saturated polyester resins, polystyrene resins, polyamide resins and polyvinyl chloride resins.

(6) The multilayered structure according to claim 3, wherein the ratio of the tensile force of the layer of the resin compositions (A) and (B) to that of the thermoplastic resin layer is 5 or less.

3. Detailed Description of the Invention

A. Industrial Field of Application

The present invention relates to a composition of a saponified product of an ethylene-vinyl acetate copolymer (referred to as EVOH hereinafter) free of pinholes, cracks, localized non-uniform portions and the like during hot drawing, especially high-speed hot drawing operation, and excellent in gas barrier property, and a hot drawn, particularly high-speed hot drawn multilayered structure using the same.

B. Prior Art

Effectiveness of EVOH has been recognized in the field of wrapping films for foodstuffs, etc., especially for the purposes of wrapping foodstuffs requiring barrier properties against oxygen, other products requiring retention of flavor, and the like. However, a film composed of EVOH alone is inadequate both in toughness and in barrier properties against water and moisture.

In order to overcome these drawbacks, EVOH has been used in the form of a multilayered structure obtained by laminating with a thermoplastic resin such as polypropylene, polystyrene, etc. and various heat sealant layers represented by those of ionomers, ethylene-vinyl acetate copolymers, etc.

In the case where multilayered structures (films, sheets, parisons, etc.) prepared by various methods are subjected to secondary forming into containers, etc., particularly in the case where drawing is performed at a temperature equal to or lower than the melting point of EVOH, small voids, cracks, localized non-uniform portions, etc. often occur in the EVOH layer so that the oxygen barrier properties of the container so formed are seriously reduced. In addition, the container does not exhibit an esthetic appearance. Accordingly, under these circumstances, EVOH cannot be used as containers for foodstuffs, etc.

For the purpose of preventing pinholes, cracks, etc. to be occurred upon hot drawing in the EVOH layer, studies have been conducted for the addition of various plasticizers into EVOH (Japanese patent Laid-open No. 53-88067 and Japanese patent Laid-open No. 59-20345), and for the blending of polyamide resins with EVOH (Japanese patent Laid-open No. 52-141785, Japanese patent Laid-open No. 58-154755 and Japanese patent Laid-open No. 58-36412), etc. In any case, however, satisfactory results were not obtained in view of the following points. In order to improve the hot drawing properties of the EVOH using plasticizers represented by those containing hydroxy groups or aromatic sulfonamides, etc., it is necessary to incorporate 10 to 20 parts by weight of the plasticizers per 100 parts by weight of EVOH. In such case, there result many problems such as vigorous reduction of gas barrier properties, reduction of the adhesion strength of the EVOH layer to other resin layers presumably due to bleeding of the plasticizers, etc. Therefore, those are inadequate for use.

Methods comprising blending polyamide resins with EVOH to impart flexibility thereto and improve secondary fabrication properties are known, and many patent applications directed thereto have been filed (Japanese published examined application No. 44-24277, Japanese published examined application No. 60-24813, Japanese

patent Laid-open No. 58-129035, Japanese published examined application No. 54-38897 and Japanese patent Laid-open No. 58-36412, etc.). However, use of polyamides, which may improve high-speed hot draw formability, produce formed products in which a large number of gel-like matters are present, presumably due to an intense chemical reaction with EVOH. Also, due to marked coloration, they have generally been found unsatisfactory for use. On the other hand, patents directed to blends of a polyamide resin and EVOH having relatively less gel and coloration have also been published. It appears that low-speed hot drawing would produce well formed products free from cracks, pinholes, non-uniform portions, etc., in view of their appearance, however, presumably due to insufficient compatibility with EVOH, the blends produce, as measured by measurement of the gas barrier properties, extremely variable data. It is suspected that the presence of minute pinholes that are hardly discernible by the naked eye is responsible. Furthermore, with the speed up of a hot drawing machine, the variation in the measurement data of gas barrier properties is greatly increased. This has resulted in reducing the reliability of these containers as ones with gas barrier properties.

Recently, there has been demand for remarkably improving gas barrier properties required to extremely prolong preservation of foods. Therefore, there is a

tendency to use the EVOH layer while increasing the thickness. In this case, very small pinholes, cracks, localized non-uniform portions and the like tend occur as compared with the use of a relatively thin EVOH layer in hot drawing, and variation in measured values for the gas barrier properties is greatly increased to result in vigorous decrease of reliability as a container with gas barrier properties.

Further, there is a tendency to blend scraps, such as trimmings from the formation process, failed containers and the like, with the thermoelastic resin material in order to reduce product costs. In this case, the thermoplastic resin layer blended with the recovered products tends to exhibit localized non-uniform portions, cracks and the like upon drawing, and becomes poor in appearance.

In addition, Japanese patent Laid-open No. 52-101182 discloses that a multilayered container excellent in barrier properties and adhesion properties is obtained by laminating a polyolefin to at least one surface of a layer of a mixture prepared by adding from 0.5 to 5 parts by weight of EVOH having an ethylene content of from 50 to 90 mol% and degree of saponification of 50 to 95 mol% to from 95 to 99.5 parts by weight of EVOH having an ethylene content of 50 mol% or less and a degree of saponification of 96 mol% or more. However, even if the layer of the mixture of EVOHs as described here is

laminated to a PP (polypropylene) layer and subjected to hot drawing, it is difficult to prevent the occurrence of small pin holes, cracks, and localized non-uniform portions. It is apparent from Comparative Example to be described below.

Therefore, it is one of important subjects to develop EVOH having good gas barrier properties and good reliability (with less un-uniformity) as containers with gas barrier properties, namely, to develop EVOH having good forming properties and causing no minute pinholes, cracks, non-uniform portions, etc. in the EVOH layer upon high-speed hot drawing.

C. Problems that the Invention is to Solve

EVOH has various excellent properties. However, when a laminate with a thermoplastic resin is subjected to secondary fabrication into containers or the like, cracks, pinholes, localized non-uniform portions, etc. occur in the EVOH layer, which greatly deteriorates the gas barrier properties. In this case, the appearance is also poor and the product cannot be used as a food packaging container.

Thus, the present inventors have extensively investigated in order to develop an EVOH composition for use in multilayered containers with no deterioration of the high gas barrier properties possessed by EVOH, and free of the occurrence of cracks, pinholes, localized non-uniform portions, etc. in the EVOH layer caused when

the laminate is secondary fabricated into containers, etc., to provide a high gas barrier properties, and as a result, they have completed the invention.

D. Means for Solving the Problems

The present invention directed to a resin composition comprising from 94 to 30 parts by weight of a saponified product(A) of an ethylene-vinyl acetate copolymer having an ethylene content of from 20 to 45 mol%, and a degree of saponification of the vinyl acetate component of 96 mol% or more, and from 6 to 70 parts by weight of a saponified product(B) of an ethylene-vinyl acetate copolymer having an ethylene content of from 24 to 49 mol%, and a degree of saponification of the vinyl acetate component of less than 96 mol%, and satisfying the following formulas (I) to (III):

Ethylene content of (B) - Ethylene content of (A) \geq 4 mol% ... (I)

Degree of saponification of (A) - Degree of saponification of (B) \geq 3 mol% ... (II), and

$1.5 + \{50 - \text{Ethylene content of (B)}\} \times 0.06 \geq |\text{SP(A)} - \text{SP(B)}|$
 $> \{\text{Ethylene content of (B)} - 38\} \times 0.04 + 0.1$... (III)

provided that

SP(A)... Solubility parameter of A (according to Small's equation)

SP(B)... Solubility parameter of B (according to Small's equation), and

a multilayered structure having a thermoplastic resin layer on at least one surface of a layer of the resin composition.

E. Detailed Description of the Invention

The present invention will be explained more in details below.

EVOH(A) and (B) used in the present invention has an ethylene content of 20 to 45 mol%, preferably 25 to 45 mol%, and a saponification degree of the vinyl acetate component of 96% or more. When the ethylene content is less than 20 mol%, the formed product temperature approaches a decomposition temperature so that the forming of a product becomes difficult. On the other hand, when the ethylene content exceeds 45 mol%, the gas barrier properties are lowered so that the gas barrier properties of the container having a multilayered structure are insufficient, which is not preferred. Furthermore, EVOH in which the saponification degree of the vinyl acetate component is less than 96 mol% is not preferred because the gas barrier properties thereof are insufficient, although such EVOH does produce a container with minimal, or no cracks, pinholes, etc. upon forming of the container.

EVOH(B) has an ethylene content of from 24 to 49 mol%, preferably, from 26 to 48 mol%, and a saponification degree of the vinyl acetate component of less than 96 mol%, preferably, less than 95 mol%. When

the ethylene content exceeds 49 mol%, not only gas barrier properties are lowered but also it is disadvantageous from a viewpoint of manufacturing cost. When it is less than 24 mol%, gel-like matters are mixed into the formed product to result in poor appearance and deterioration of gas barrier properties. When the degree of saponification of the vinyl acetate exceeds 96 mol%, it is difficult to obtain an excellent multilayered structure with polyethylene terephthalate, etc. other than PP although it is possible to obtain excellent multilayered structures with PP. Further, EVOH(A) and EVOH(B) each have a melt viscosity index of 0.1 to 25 g/10 min, preferably, from 0.3 to 20 g/10 min as measured according to ASTM-D-1238-65T at 190°C under a load of 2160 g.

In the invention, it is important to satisfy the formulas (I), (II) and (III) described above. When the ethylene content of EVOH(B) - the ethylene content of EVOH(A) is less than 4 mol%, or when the degree of saponification of EVOH(A) - the degree of saponification of EVOH(B) is less than 4 mol%, cracks tend to occur, and the uneven thickness may be increased, or the measured values for the gas barrier properties vary, which is problematic in reliability of containers having gas barrier properties. However, even when the difference of the ethylene content between EVOH(A) and EVOH(B) is 4 mol% or more, and the difference between

the degree of saponification of EVOH(A) and that of EVOH(B) is 3 mol% or more, external defects such as cracks, unevenness, etc., or large variation in gas barrier properties occur depending on the combination in some cases. Then, the present inventors have extensively investigated in details, and to their surprise, they have found that when the difference between the solubility parameter SP(A) of EVOH(A) and the solubility parameter SP(B) of EVOH(B) is within a range shown in the following formula, containers free of external defects such as cracks, unevenness, etc., and exhibiting less variation in the gas barrier properties can be obtained, and have accomplished the invention.

$$1.5 + \{50\text{-Ethylene content of (B)}\} \times 0.06 \geq |SP(A) - SP(B)| \\ > \{ \text{Ethylene content of (B)} - 38 \} \times 0.04 + 0.1.$$

By the way, the difference between SP(A) and SP(B) exceeds $1.5 + \{50\text{-Ethylene content of (B)}\} \times 0.06$, the compatibility between EVOH(A) and EVOH(B) is lowered, and presumably because generation of fine voids occurs by exfoliation of the boundary between EVOH(A) and EVOH(B), the variation in the gas barrier properties increases. On the other hand, the difference between the SP(A) and the Sp(B) is smaller than $\{ \text{Ethylene content of (A)} - 38 \} \times 0.04 + 0.1$, presumably due to abnormal dispersion of particles, unevenness tends to occur upon draw-molding.

The preferable range for (I), (II) and (III) is

described as (I'), (II'), and (III') below.

$25 \text{ mol\%} \geq \text{Ethylene content of (B)} - \text{Ethylene content of (A)} \geq 4 \text{ mol\%} \dots (\text{I}')$

$20 \text{ mol\%} \geq \text{Degree of saponification of (A)} - \text{Degree of saponification of (B)} \geq 3 \text{ mol\%} \dots (\text{II}')$, and

$1 + \{50 - \text{Ethylene content of B}\} \times 0.06 \geq |\text{SP(A)} - \text{SP(B)}| > \{\text{Ethylene content of (B)} \times 0.01 - 38\} + 0.2 \dots (\text{III}')$

Next, as for the mixing ratio (by weight) between EVOH(A) and EVOH(B), A/B is 94/6 to 30/70, preferably, 95/5 to 55/45. When the mixing ratio satisfies $A/B < 94/6$, it is not preferred since cracks, portions with uneven drawing, or pin holes tend to occur upon forming of containers, and large variation in gas barrier properties occurs upon forming containers. Meanwhile, when $A/B > 30/70$ is satisfied, localized non-uniform portions occur, which is not preferred in view of appearance. The preferred range thereof is $93/70 \geq A/B \geq 60/40$.

In the present invention, it is preferred that EVH(A) and EVOH(B) satisfy the following formulas (IV) to (VI).

$E'(B) \leq 10^9 \text{ dyne/cm}^2 \dots (\text{IV})$

$1 \leq E'(A)/E'(B) \dots (\text{V})$

$0.05 \leq \text{MI(A)}/\text{MI(B)} \leq 20 \dots (\text{VI})$

$E'(A) \dots$ Dynamic viscoelasticity of A (dyne/cm²) at hot drawing temperature - 10°C

$E'(B) \dots$ Dynamic viscoelasticity of B (dyne/cm²) at a hot

drawing temperature

MI(A) ... Melt index of A at 190°C under 2160 g load
(g/10 min)

MI(B) ... Melt index of B at 190°C under 2160 g load
(g/10 min)

In the case where $MI(A)/MI(B)$ is less than 0.05 or where it is more than 20, or in the case of $E'(A)/E'(B) < 1$, localized non-uniform portions tend to occur upon forming of containers. While the dynamic viscoelasticity is greatly affected by the ethylene content and the degree of saponification of EVOH, when $E'(B)$ exceeds 10^9 dyne/cm², cracks or pinholes tend to occur upon forming of containers.

The method of blending EVOH(A) and EVOH(B) is not particularly limited. There is a method which comprises dry-blending EVOH(A) and EVOH(B), pelletizing the blend using a Banbury mixer, a single-or twin-screw extruder, etc. and then drying the pellets, or the like. When the blend is heterogeneous or gel and hard spots occur or mixed during the blending operation, it is highly likely that breakage and unevenness of the EVOH blend layer occur upon hot drawing. Therefore, it is preferred that an extruder having a high kneading degree is used, the opening of a hopper is sealed with N₂ and the extrusion is performed at low temperatures, upon blending with heating using an extruder.

Additionally, other additives (various resins,

antioxidants, plasticizers, coloring agents, etc.) can be freely used within a range which does not inhibit the effect and function of the present invention, upon mixing them. In particular, for the purposes of stabilizing resins against heat and preventing the occurrence of gels, it is advantageous to incorporate 0.01 to 1 wt% of a hydrotalcite type compound, or a hindered phenol type or hindered amine type stabilizer.

Although the EVOH composition of the present invention can be formed into a film, sheet, tube, bottle and the like by well known melt molding and compression molding techniques, the composition can exhibit its features most effectively when used as one layer of the a multilayered structure. This point is explained below.

The thermoplastic resin used in the present invention may be any resin that can be drawn and formed at temperatures described below. Preferred examples of such resin include polypropylene resins, saturated polyester resins, polystyrene resins, polyamide resins, and polyvinyl chloride resins. Among them, polypropylene resins (homopolypropylene, block copolymer polypropylene with ethylene, random copolymer polypropylene, etc.) polystyrene resins and polyester resins are most preferred.

When the melting point of EVOH(A) is designated $X^{\circ}\text{C}$, and the temperature of the thermoplastic resin upon hot

drawing is designated $Y^{\circ}\text{C}$, the following equation can be satisfied:

$$X-10 \geq Y \geq X-110$$

When Y is higher than $(X-10)^{\circ}\text{C}$, EVOH is softened and melts upon forming so that the formed product can generally be effected even though no additive is incorporated. On the other hand, when Y is lower than $(X-110)^{\circ}\text{C}$, the glass transition temperature (T_g) of the thermoplastic resin becomes lower than a room temperature so that the formed product exhibits a seriously unstable shape at a room temperature with great dimensional change and which is therefore, not usable.

To obtain the multilayered structure, there are many applicable methods including a method which comprises laminating the EVOH composition on the thermoplastic resin via an adhesive resin by an extrusion laminate method, a dry laminate method, a co-extrusion laminate method, a co-extrusion sheet preparation method (feed block or multi-manifold method, etc.), a co-extrusion pipe preparation method, a co-injection method, various solution coating methods, etc. to give a laminate, then reheating and drawing the laminate within a temperature range at or lower than the melting point of the thermoplastic resin using, for example, a vacuum and pressure deep drawing machine, a biaxially drawing blower, etc. (SPPF molding) or melt-molding the laminate at or higher than the melting temperature of

the thermoplastic resin; or a method which comprises subjecting the aforementioned laminate (sheet or film) to hot drawing by a biaxially drawing machine; or a method which comprises biaxially drawing the EVOH composition and the thermoplastic resin while co-injecting them, etc.

As for the thickness of the multilayered structure, a multilayered structure having a ratio of the tensile force of the EVOH layer to that of the thermoplastic resin layer of about 5 or less, preferably about 1 or less at a hot drawing temperature can produce favorable molding products. When the tensile force ratio is 5 or more, even the EVOH composition is liable to produce unfavorable cracks, unevenness, etc.

The tensile force of the thermoplastic resin layer in the multilayered structure herein described is measured at 50 mm/min of tensile rate, being 50 mm of chuck distance, at 100% elongation, at the same temperature as the hot drawing temperature. The tensile force of the EVOH layer is that of a monolayered EVO comprising a blend of EVOH(A) and EVOH(B) measured under the same condition as described above. These tensile forces can also be measured under the same condition as described above on a multilayered structure after hot drawing, subjected to hot press, and relaxed the draw to be returned to the state before hot drawing.

The construction of the multilayered structure can

include, as representative examples, thermoplastic resin/EVOH composition/thermoplastic resin, EVOH composition layer/adhesive resin layer/thermoplastic resin layer, and thermoplastic resin layer/adhesive resin layer/EVOH composition layer/adhesive resin layer/thermoplastic resin layer. When forming the thermoplastic resin layer on both outer sides, they may be the same or different resins. The adhesive resin as used herein refers, with no particular restriction, to any resin which is capable of drawing at temperatures equal or lower than the melting point of EVOH and can adhere the EVOH composition layer to the thermoplastic resin layer. Preferred adhesive resins include polyolefins (e.g., polyethylene, polypropylene), ethylene-vinyl acetate copolymers, ethylene acrylic acid ester (e.g., methyl ester, ethyl ester) copolymers, and the like, having added or grafted thereto ethylenically unsaturated carboxylic acids or anhydrides thereof (e.g., maleic anhydride).

In the present invention, the hot drawn multilayered structure includes containers such as cups, bottles, etc., or sheets or films obtained by hot drawing, as described above. Furthermore, hot or heating refers to any method for allowing the multilayered structure to stand at temperatures necessary for hot drawing for a definite period of time and operating the multilayered structure so as to be substantially thermally uniform.

A method of heating to make thermally uniform structures using various heaters is preferred taking operability into account. The hot or heating operation may be performed at the same time as the drawing or may be performed prior to the drawing. The term "drawing" refers to the operation of forming a uniformly heated multilayered structure into a container, a cup, a sheet or a film by a chuck, a plug, vacuum and pressure forming, blowing, etc. Both monoaxial drawing and biaxial drawing (simultaneous or sequential) can be used. A draw ratio and a drawing speed can be appropriately selected depending upon the purpose, but in the present invention, "high-speed drawing" means a method for uniformly forming a container or a film at a drawing speed (area magnification) as high as 5×10^5 %/min or more, but it is not always necessary that the formed product be oriented.

The draw ratio, based on area, should be about 70 times or less, preferably about 36 times or less. When the draw ratio is 70 times or more, the thermoplastic resin cannot be drawn uniformly, and satisfactory multilayered structures do not liable to be obtained.

The moisture content of the EVOH composition layer, as one structural body of the multilayered structure upon hot drawing is not particularly limited, but preferably is in the range of from about 0.01 to about 10 percent.

The recovery of the trimming resulted upon forming

of containers and scraps of defective containers and the like is not particularly limited. The scraps may be recovered by a method of pulverizing, drying when moistened, and dry blending with a raw material thermoplastic resin; a method of pelletizing pulverized scraps and dry blending them with a raw material thermoplastic resin; and a method of blending and pelletizing pulverized scrap and a raw material thermoplastic resin. With respect to a blend ratio of the scrap to the raw material thermoplastic resin, as the ratio of the scrap is increased, unfavorable phenomena such as occurrence of localized non-uniform properties upon draw molding, unevenness, cracks, haze and the like are liable to occur. Generally, a blend ratio in the range of about 2 to 40 percent is acceptable, although it depends on the forming conditions. Plural additives such as maleic acid anhydride modified polyolefins, metal soaps, hydrotalcite compounds and the like are preferably added to improve the dispersibility and thermal stability, and to prevent unfavorable phenomena during the forming of the container.

The thus obtained high-speed thermodrawn multilayered structure, exhibiting excellent gas barrier properties and free from pinholes, cracks and localized non-uniform portions, is effective for use as a uniform high quality packaging container having excellent gas barrier properties for foods and a

container which retains fragrances and the like.

The present invention will be further explained with reference to examples, but it should not be construed that the invention is limited only to these Examples.

F. Example

Example 1

EVOH(A) ("EP-E101" manufactured by KURARAY CO., LTD.) having an ethylene content of 32 mol%, a degree of saponification of 99.6 mol%, and a melt index (MI at 190°C) of 1.6 g/10 min was found to have a solubility parameter (SP(A)) of 12.3 and a dynamic viscoelasticity ($E'(A)$ at 120°C) of 7×10^{10} dyne/cm² measured using a Vibron (manufactured by Toyo Baldwin Co., Ltd.). On the other hand, EVOH(B) having an ethylene content of 44 mol%, and a degree of saponification of 91 mol%, and a melt index (MI(B) at 190°C) of 5.5 g/10 min was found to have a solubility parameter (SP(B)) of 11.4, the ethylene content of (B) is greater than the ethylene content of (A) by 12 mol%, the degree of saponification of (A) is greater than the degree of saponification of (B) by 8.6 mol%, and further, the difference between SP(A) and SP(B) was 0.9. Further, the dynamic viscoelasticity ($E'(B)$ at 130°C) was 8×10^8 dyne/cm², and the ratio of the $E'(B)$ to $E'(A)$, namely, ($E'(A)/E'(B)$) was 88.

Those EVOH(A) and EVOH(B) were mixed at a weight ratio (A)/(B) of 80/20, and then pelletized using a

twin-screw type vented 40 mm ϕ extruder at 200°C in an N₂ atmosphere. The pellets obtained were dried at 80°C for eight hours. The pellets were then fed to a feed block type coextruder of 5 layers with 3 extrudates to form a sheet. The sheet thereby obtained was constructed of both outer layers of 800 μ m made of polystyrene ("ET-61" manufactured by Idemitsu Styrol), adhesive layers of 50 μ m ("Merthene M-5420", manufactured by Toyo Soda Mfg. Co., Ltd.), and an innermost layer of 50 μ m (at the center) made of the above-mentioned EVOH. The tensile force of the obtained polystyrene layer of this sheet was measured at 150°C, and it was found that the tensile force at 100% elongation was 0.4 kg/15 mm width. In addition, the tensile force of the EVOH layer (50 μ m) was found to be 0.2 kg/15 mm width under the same conditions. That is, the ratio the tensile force of EVOH layer/polystyrene layer was 0.5.

The sheet was subjected to thermoforming by a vacuum and pressure forming machine (at a draw speed of $9 \times 10^5\%$ (area magnification)/min, a draw ratio of 1 (stretch factor: 7 times) at 130°C. The formed articles thus obtained were excellent in clarity and appearance and did not exhibit cracks or localized non-uniform portions. The gas barrier properties of these containers were measured at 20°C, 65% RH using 10/50 type of MOCON Inc. to find that the oxygen permeation amount thereof was 0.7 cc \cdot 20 μ m/m² \cdot 24 hr \cdot atm, which was extremely

excellent gas barrier property, and the variation of measured values when measurement was conducted for 20 samples ($R = \text{maximum value} - \text{minimum value}$) was as extremely small as $0.2 \text{ cc} \cdot 20 \mu\text{m}/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$. Thus, they were containers with excellent barrier properties.

Comparative Example 1

Formed articles were produced in the same manner as Example 1 except that EVOH(B) used in Example 1 was replaced with an EVOH(B) having an ethylene content of 44 mol% and a degree of saponification of 99.4 mol%. The formed containers thus obtained cannot be put to practical use in view of appearance because the formed containers exhibited many locally non-uniform portions and cracks.

Example 2

A blend of EVOH(A) and EVOH(B) used in Example 1 was prepared and formed into a container of 3 layers with 2 extrudates, constructed of polyester ($[\eta]=0.70$)/a blend of EVOH(A) and EVOH(B)/polyester ($[\eta]=0.70$) using a coinjection costretch blow molding machine manufactured by NISSEI ASB MACHINE CO., LTD. (at a draw temperature of 100°C , drawing speed of $5 \times 10^5\%$ (area magnification)/min, and a stretch factor of 10 times). As a result, bottle containers free of longitudinal strips of localized uneven thickness, localized non-uniform portions, cracks and the like, exhibiting excellent gas barrier property (oxygen permeation amount

of 0.5 cc·20 $\mu\text{m}/\text{m}^2\cdot 24 \text{ hr}\cdot\text{atm}$, $R = 0.1 \text{ cc}\cdot 20 \mu\text{m}/\text{m}^2\cdot 24 \text{ hr}\cdot\text{atm}$) were obtained.

The dynamic viscoelasticity in this case was that $E'(A)90^\circ\text{C} = 9 \times 10^{10} \text{ dyne}/\text{cm}^2$, $E'(B)100^\circ\text{C} = 9.9 \times 10^8 \text{ dyne}/\text{cm}^2$. The tensile force of the polyester layer of parisons before hot drawing was 2.8 kg/15 mm width at 100°C , and the tensile force of the EVOH layer was 0.5 kg/15 mm width. Namely, the ratio of a tensile force of the EVOH layer to that of the polyester layer was 0.18.

Comparative Example 2

Formed articles were produced in the same manner as Example 6 except that only EVOH(A) was used. The thus obtained formed bottles could not be put to practical use in view of the appearance because the bottles exhibited a large number of longitudinal strips of localized uneven thickness, and localized non-uniform portions.

Example 3

EVOH(A) having an ethylene content of 32 mol%, a degree of saponification of 99.6 mol%, and a melt index (MI at 190°C) of 1.5 g/10 min was found to have a solubility parameter (SP(A)) of 12.4 and a dynamic viscoelasticity ($E'(A)$ at 140°C) of $3 \times 10^9 \text{ dyne}/\text{cm}^2$. On the other hand, EVOH(B) having an ethylene content of 40 mol%, a degree of saponification of 94.5 mol%, and a melt index (MI(B) at 190°C) of 5.0 g/10 min was found to have a solubility parameter (SP(B)) of 11.7. The

ethylene content of (B) was greater than the ethylene content of (A) by 8 mol%, the degree of saponification of (A) was greater than the degree of saponification of (B) by 4.6 mol%, and further, the difference between SP(A) and SP(B) was 0.7. Further, the dynamic viscoelasticity ($E'(B)$ at 150°C) was 1×10^8 dyne/cm², and the ratio of $E'(A)$ to $E'(B)$, namely, ($E'(A)/E'(B)$) was 30.

Those EVOH(A) and EVOH(B) were mixed at a weight ratio (A)/(B) of 90/10, and the blend was palletized and a sheet was formed in the same manner as in Example 1. The sheet was constructed of both outermost layers of 800 μm made of polypropylene (Mitsubishi Noblen MA6), adhesive resin layers of each 50 μm (Admer QF500", manufactured by Mitsui Petrochemical Co., Ltd., and further an innermost layer (at the center) of 50 μm made of the EVOH layer described above.

A tensile force of the PP layer of the obtained sheet at 150°C was 1.6 kg/15 mm width, and a tensile force of the mono-layer EVOH (50 μm) at 150°C was 0.2 kg/15 mm width. Namely, the ratio of the tensile force between the EVOH layer/the PP layer was 0.13. The sheet was subjected to thermoforming (SPPF molding) by a vacuum and pressure forming machine (at a drawing speed of $9 \times 10^5\%$ /min, draw ratio of 1 (stretch area magnification: 7 times) at 150°C . The formed articles thus obtained were excellent in clarity and appearance and did not exhibit cracks or

unevenness.

The gas barrier properties of these containers at 20°C, 65%RH were excellent such that the oxygen permeation amount was 0.6 cc·20 $\mu\text{m}/\text{m}^2\cdot 24 \text{ hr}\cdot\text{atm}$. In addition, the variation (R) of measured values when measurement was conducted for 20 samples was extremely as small as 0.2 cc·20 $\mu\text{m}/\text{m}^2\cdot 24 \text{ hr}\cdot\text{atm}$. Thus, they were containers with excellent barrier properties.

Comparative Example 3

Formed articles were produced in the same manner as Example 3 except that EVOH(A) used in Example 3 was replaced with an EVOH(A) having an ethylene content of 37 mol%, a degree of saponification of 99.6 mol%, and a melt index (MI at 190°C) of 1.5 g/10 min. The solubility parameter of the EVOH(A) was 12.1, and dynamic viscoelasticity thereof was $2 \times 10^{10} \text{ dyne}/\text{cm}^2$. The thus obtained formed containers could not be put to practical use in view of appearance because the containers exhibited much unevenness.

Example 4

Formed articles were produced in the same manner as in Example 3 using a resin prepared by pulverizing trimmings and scraps of the multilayered structure generated during the forming of the containers of Example 3 and palletizing them, blending the palletized resin with polypropylene resin (MA6) in an amount of 30 %. Then, excellent containers free of cracks and unevenness could

be obtained, even though they had a structure that recovered substances, such as trimmings, scraps and the like were incorporated in the PP layer. They were containers with excellent gas barrier properties in which an O₂ gas barrier property was as low as 0.7 cc·20 μm/m²·24 hr·atom, with less variation (R) of the measured values being as small as 0.1 cc·20 μm/m²·atom.

Comparative Example 4

Formed articles were produced in the same manner as Example 3 except that EVOH(B) used in Example 3 was replaced with an EVOH(B) having an ethylene content of 59 mol%, a degree of saponification of 70 mol%, and a dynamic viscoelasticity E' of 10⁸ dyne/cm² or less (at 150°C). As a result, the formed containers exhibited a lot of gels, the variation (R) in measured values on gas barrier properties (measured for 20 samples) was as large as 18 cc·20 μm/m²·24 hr. Thus, the containers could not be put to practical use.

Comparative Example 5

Formed articles were produced in the same manner as Example 3 except that EVOH(B) used in Example 3 was replaced with an EVOH(B) having an ethylene content of 37 mol%, a degree of saponification of 50 mol%, and a dynamic viscoelasticity E' of 10⁸ dyne/cm² or less (at 140°C). In this case, SP(A) of EVOH(A) was 10.0, and |SP(A)-SP(B)| was as large as 2.4. As a result, the formed containers exhibited gel-like matters, and the variation

(R) in measured values on gas barrier properties (measured for 20 samples) was as large as $12 \text{ cc} \cdot 20 \text{ } \mu\text{m}/\text{m}^2 \cdot 24 \text{ hr.}$ Thus, the containers could not be put to practical use.

Comparative Example 6

Formed articles were produced in the same manner as Example 3 except that EVOH(A) used in Example 3 was replaced with an EVOH(A) having an ethylene content of 22 mol%, a degree of saponification of 99.6 mol%, and a SP(A) of 12.7 and further, the EVOH(B) was replaced with an EVOH(A) having an ethylene content of 28 mol%, a degree of saponification of 95 mol%, and SP(B) of 12.3. In this case, $|\text{SP(A)} - \text{SP(B)}|$ was as small as 0.4. As a result, the formed articles exhibited a large number of cracks and unevenness, and thus they could not be put to practical use.

G. Advantage of the Invention

A multilayered structure obtained from the resin composition according to the invention exhibits less cracks and uneven thickness, and is excellent in gas barrier properties with less variation in the gas barrier properties.

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